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Project Title: Assessment of PAH in Detroit and Cuyahoga River Sediments

Project Category: Contaminated Sediments

Rank by Organization (if applicable): 0

Total Funding Requested ($): 179,515 **Project Duration:** 1.5 Years

Abstract:

Currently, assessments of contaminated sediments are expensive and slow due to detailed sampling and analysis requirements, and are therefore limited in spatial resolution. Remediation efforts resulting from these sediment assessments can be made more focused and therefore less costly if higher resolution assessments of not only present loads of contaminants but also sources of contaminants were possible. The Organic Geochemistry Laboratory at the University of Massachusetts Boston proposes high resolution assessments of sediments in two areas of concern (AOCs) in Lake Erie, Detroit River and Cuyahoga River, both historically impacted by polycyclic aromatic hydrocarbons (PAH). We will use time-resolved laser-induced fluorescence (TR-LIF) spectroscopy to make high resolution pyrene measurements in sediment porewaters. Pyrene will serve as a measure of total PAH, the expected metric for PAH toxicity under new sediment quality guidelines. Additionally, we propose to incorporate the high resolution measurements into a contaminant fate model that along with proposed seasonal source (atmosphere, rivers) measurements should make the assessment applicable to other hydrophobic contaminants such as polychlorinated biphenyls (PCBs). We expect this combination of measurements and modeling will rapidly and precisely identify the most critical sediments for remediation.

Geographic Areas Affected by the Project

States:

- ☐ Illinois
- ☐ Indiana
- ☒ Michigan
- ☐ Minnesota
- ☐ New York
- ☐ Pennsylvania
- ☐ Wisconsin
- ☒ Ohio

Lakes:

- ☐ Superior
- ☐ Huron
- ☐ Michigan
- ☒ Erie
- ☐ Ontario
- ☐ All Lakes

Geographic Initiatives:

☐ Greater Chicago ☒ NE Ohio ☐ NW Indiana ☐ SE Michigan ☐ Lake St. Clair

Primary Affected Area of Concern: Detroit River, MI

Other Affected Areas of Concern: Cuyahoga River, OH

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

Polycyclic aromatic hydrocarbons (PAH) are a class of organic compounds containing a number of carcinogenic and mutagenic entities. The PAH have been and continue to be of major concern in contaminated sediments, a situation reemphasized in the GLNPO request for proposals (RFP) and specifically identified in the Lake Erie LaMP. While the costs of contaminated sediment cleanup (e.g dredging) are seemingly straightforward, the question of how much must be cleaned up is determined by sediment assessments based on discrete samples. The classical methods of PAH detection and quantification, gas chromatograph (GC) and GC-Mass Spectrometry (MS), are expensive and time consuming and as a result limit the number of samples usually taken at any particular site. For example, in what was considered a very extensive assessment of the Cuyahoga River, 90 samples were analyzed for the entire area of concern. Since PAH distributions have often been shown to be heterogeneous, this limited sampling leaves open to question the overall assessment of a particular site. While the RFP notes that the remediation of contaminated sediments is of particular concern, PAH deposition is not only an historical issue but also a current one. The source of PAH to aquatic sediments is primarily combustion with a generally small contribution from petrogenic sources. PAH continually arrive in lake and estuarine areas as a result of atmospheric deposition and riverine transport. Our recent study of Boston Harbor indicates that PAH continue to accumulate in the sediments even after dramatic point source reductions of contaminants such as PCBs and dioxins.

It is therefore important not only to have better maps of identified contaminated sites but also to have a wider assessment of potentially contaminated areas. A model incorporating the sources of contaminants for specific shoreline and river areas based on temporally and spatially intensive sampling of PAH in multiple media - sediments, overlying water, riverine and atmospheric - would vastly improve these contaminated sediment assessments. Incorporating high resolution chemical data directly into a caontaminant fate model would improve the decision-making process. Improved high-resolution assessments, would thus focus cost-effective remediation efforts to the contaminated "hot spots" reducing costs of, for instance, large scale dredging operations.

Proposed Work Outcome:

Proposed Work

The Organic Geochemistry Laboratory of the University of Massachusetts Boston proposes to apply time-resolved, laser-induced fluorescence (TR-LIF) spectroscopy for the detection of pyrene in porewaters to provide a high resolution surface sediment map of polycyclic aromatic hydrocarbon (PAH) contamination in the Detroit River and the Cuyahoga River areas of concern. In addition to sediment porewater measurements, PAH will be simultaneously quantified in overlying water, local riverine sources, and the local atmosphere to derive a model of PAH sources and deposition in these areas. These high-resolution assessments can be used to guide sediment remediation efforts, and the methods used in this study

can be applied to assessments of other Great Lakes areas of concern.

Approach

The TR-LIF method preferentially detects pyrene as a result of its distinctively long fluorescence lifetime in aqueous media. Briefly, a short N2 laser pulse excites a fluorescent molecule to its excited state, and depending on the individual fluorophore, a photon is emitted a characteristic lifetime (1-150 ns) later. By using fast (ns) electronics and fiber optics, pyrene (128 ns) can be differentiated from background natural organic substance (humic) fluorescence (1-10 ns). This major breakthrough (Rudnick and Chen, 1998) allows the rapid analysis of environmental contaminants in situ. The current UMassBoston TR-LIF system is capable of in situ pyrene quantification with a detection limit of ~5 ng/l (parts per trillion) which is more than sufficient for ambient water column and porewater monitoring of most coastal areas (Boston Harbor porewaters have pyrene levels of 20 -400 ng/l and water column pyrene levels of 10 - 50 ng/l). Using a fiber optic probe located directly in the water, the TR-LIF system can take water column measurements approximately every 20 seconds. For sediment work, the speed of measurement is dictated by the physical sampling mechanism. For porewater sampling, simple surface grab samples can be squeezed, and pyrene analysis is essentially instantaneous. We expect to be able to make sediment grabs every 30 m or so in a contaminated area about once every 10 minutes so that ~50 samples can be analyzed in a day. Additionally, data is acquired on board ship so that porewater analyses can be used to effectively guide sampling strategies to the highest priority areas.

PAH in sediments has been found to partition into a biologically available fraction and an unavailable fraction. Thus sediment PAH levels are not directly responsible for many of the biological effects seen in benthic organisms. Sediment porewater measurements are being found to be, in fact, a better measure of the toxic potential of contaminated sediments than total sediment contaminant concentrations. The current problem is lowering analytical detection limits so that reasonable volumes of porewater can be routinely obtained and analyzed. Our TR-LIF system has sufficient sensitivity to analyze porewaters directly without concentration or extraction.

The composition of the total mixture of PAH found in the environment is fairly constant. A compilation of seven previous studies of sediment PAH levels, encompassing seventy-two discrete samples, indicated that pyrene occurs at a consistent mean level of 10.5 +/- 1.0 % of the total PAH at a confidence level of 95%. The same studies indicate a mean ratio of pyrene to benzo[a]pyrene (BaP), a carcinogenic PAH of particular concern, of 3.3 +/- 1.7, again at the 95% confidence level. Therefore pyrene can be used to estimate both BaP and total PAH in sediment porewaters.

For atmospheric PAH inputs, we will use a large volume sampling system consisting of polyurethane foam (PUF) filters, organic solvent extraction, and analysis by TR-LIF. Pyrene also has a long characteristic lifetime in dichloromethane so that it can be analyzed directly in the extract. We can therefore minimize the need for time-consuming procedures such as GCMS to determine pyrene levels. We propose to utilize this capability in addition to the water column and porewater capabilities of our system by combining it with a low solvent extraction method developed by Maddalena et al (1998) withEPA funding to provide analyses of air concentrations of pyrene to help complete the a source model.

Proposed Work

The investigation will consist of a detailed sediment survey in year one and 3 additional efforts (seasonal) for riverine and atmospheric sampling. 5 days of sediment analyses (up to 50 samples per day) at each site (Detroit River, Cuyahoga River) will yield over 200 analyses, more than doubling the resolution of the "extensive" sediment survey being completed in the Cuyahoga River. Additionally, by analyzing sediments on board, sampling locations can be rapidly guided to high priority areas. We expect that samples every 30 m where warranted can precisely define the extent of sediment contamination. Pyrene measurements will be made on porewaters squeezed from surface sediment grab samples. A subset of the samples will be selected for preservation (freezing) and more complete analysis by GCMS at UMassBoston.

Riverine endmember samples will also be measured seasonally (four efforts) so that this data can be included in the model. The river source is expected to change seasonally with source, river flow, and temperature being the major influences on PAH concentrations in river water. While a more detailed temporal study may further refine input functions, we feel that quarterly sampling is sufficient to constrain the model and that further temporal resolution would not result in a significant changes in the outcome of the model given some of the other sources of variability.

Additionally, large volumes of air will be sampled for particulate and vapor phase PAH. Daily samples will be taken over the course of 7 days during each of the sampling efforts. This will allow us to determine day-to-day variability as well as longer term seasonal trends. A PUF sampler (Maddalena et al, 1998) will be used to extract vapor phase PAH and a

glass fiber filter will be used to extract particles. The samples will be stored for extraction in the laboratory and quantification both by TR-LIF and GCMS.

Outcomes

Detailed assessments of the sediment PAH loadings in the Detroit River and Cuyahoga River areas of concern will improve remediation efforts that have begun or are planned to begin soon in these areas. Additionally a model will be developed to predict future inputs of PAH to these areas, and these predictions can be tested with TR-LIF or traditional analysis following this project. Finally, a sediment/water/air sampling and analysis system supplying the necessary concurrent contaminant measurements for a predictive model will result. It is possible that the measurements of pyrene can be used to predict the fate of other contaminants such as PCBs or dioxins.

Budget Justification

Three key personnel are included in the preliminary budget for this proposal. R.F. Chen (.5 months requested, 1 month match), a recognized expert in environmental geochemistry who has vast experience with ship-board sampling and analysis of organic contaminants will oversee the project. S.M. Rudnick (10 months) who has a Ph.D. in environmental chemistry as well as master's and bachelor's degrees in electrical engineering will be responsible for the TR-LIF system, the field work, and laboratory analysis. One semester of a PhD candidate is requested to help on field deployments.

$15,000 of the proposed budget will support a redesign of the TR-LIF system to enhance its mobility and therefore future application. The current system costs approximately $80,000 and weighs over 100 kg. The new design will cost approximately $15,000 and weigh approximately 40 Kg so it can easily be transported from one assessment site to another. An added coastal management benefit which derives from the redesign of the TR-LIF system is the availability of an affordable system to track petrochemical spills in the water environment, the second significant source of PAH. Since pyrene occurs at .1 to 1% levels in crude oils (1 liter of oil could theoretically be tracked to a dilution of over 200 million times).

Project Milestones:	**Dates:**
Project Start	07/2000
QAPP Completed	09/2000
First Riverine and Air Sampling	11/2000
First Interim Report, 2nd Sampling	02/2001
Detailed Sediment Survey, 3rd Sampling	06/2001
Fourth Riverine and Air Sampling	09/2001
Management Debriefings	11/2001
Project End and Final Report	12/2001

☐ Project Addresses Environmental Justice

If So, Description of How:

☒ Project Addresses Education/Outreach

If So, Description of How:

An EPA envirobrief on the TR-LIF technique as well as the detailed assessments of the Detroit River and the Cuyahoga River will be created and distributed in coordination with the EPA Region 5 Environmental Education Office. Additionally, S.M. Rudnick and R.F. Chen will be available for classroom or public discussions in appropriate settings regarding this project. The results of this investigation provide an opportunity for the public discussion of PAH health and environmental issues and explorations of methods to reduce their generation.

Project Budget:

	Federal Share Requested ($)	Applicant's Share ($)
Personnel:	67,500	7,000
Fringe:	14,960	1,746
Travel:	12,000	0
Equipment:	15,000	0
Supplies:	12,000	0
Contracts:	5,000	0
Construction:	0	0
Other:	0	0
Total Direct Costs:	126,460	8,746
Indirect Costs:	53,055	5,502
Total:	179,515	14,248
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

Description of Collaboration/Community Based Support:

At the time of the preproposal, no collaborations have been made. However, should a full proposal be requested, we intend to work closely with the Cuyahoga Coordination Committee and the Cuyahoga River Community Planning Organization in the Cuyahoga River area of concern, and similar entities in the Detroit River area to maximize the utility of the sediment assessments. Previous data and current efforts will be reviewed in order to plan our air, river, and sediment measurements. Meteorological data will be gathered from appropriate NOAA weather stations, and pertinent flow data from the US Geological Survey.